Development of an on-line hot catcher for volatile species

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New isotopes of elements 112 and 114 have been produced in [48]Ca beam induced fusion reactions with [238]U and [242, 244]Pu targets [1]. Their relatively long half-lives give chemists the possibility to investigate the chemical properties of these super heavy elements. The gas-phase chemical investigation of transactinides has gained remarkable progress during the last decade. Continuously operating gas-phase separations, e.g., some devices based on the On-Line Gas chromatographic Apparatus (OLGA), were instrumental to study the formation of halide, oxohalide and hydroxide compounds of transactinides from Rf through Bh. The In-situ Volatilization and On-line detection apparatus (IVO) was successfully applied to study the volatility of the tetroxide of HsO_4 [2]. For the heaviest element, calculations of the electron configurations predicted increasingly strong relativistic effects that may strongly influence their chemical behavior. Hence, the elements 112 and 114 are predicted to be chemically inert and volatile elements, similar to noble gases [3]. On the other hand, classical extrapolations along the groups of the periodic table predict elements 112 and 114 to behave similar to their homologues in the groups 12(Zn, Cd, Hg) and 14(Ge, Sn, Pb), respectively [4]. The expected *high volatility in elemental states* would allow us the chemical investigation of these elements with gas-phase chemical methods or even better at vacuum conditions. The differentiation between either a metallic or a noble-gas character of the heaviest elements could be achieved by vacuum thermochromatography, that provide very clean surfaces in the adsorption process. It also supplies crucial advantages for the experiment with short-lived isotopes: 1) fast separation under molecular flow condition; 2) no carrier gas; 3) a very stable temperature gradient due to the good heat isolation in vacuum; 4) vacuum chemical apparatus could be friendly coupled with a physical separator.

In order to transfer the fusion-reaction products from the target position to the chemical apparatus in vacuum, an on-line hot catcher system coupled to a vacuum thermochromatographic apparatus is now being developed at Paul Scherrer Institute, Switzerland.

The working principle is as follows: Products from heavy ion induced fusion reactions have a recoil momentum sufficiently high and forward-peaked in order to penetrate the target material ($\approx$1mg/cm^2). Passing a thin carbon window ($\approx$30 μg/cm^2), they are implanted into a solid catcher, which is heated up to 2000K. Due to thermo-diffusion, the implanted atoms drift towards the surface of the catcher and desorb from the catcher surface. Subsequently, they effuse inside of the surrounding crucible until they pass the inlet to the thermochromatographic device.

The yields and velocities of the described processes are closely related to the material constants of the solid catcher and of the crucible material, such as diffusion coefficients and adsorption enthalpies. Hence, in order to find the proper catcher material to release volatile metallic p-elements rapidly with high efficiency and also to investigate their adsorption behavior on different metal surfaces by means of vacuum thermochromatography, off-line experiments based on the long–lived isotopes of Tl, Pb, and Bi were performed. An off-line model set-up for "hot catcher" test experiments (see Fig.1) was developed. Isotopes of the p-elements Bi, Pb, Tl were produced by bombarding a [nat.]W(9 μm) target foil with a [20]Ne beam (110 MeV on the target) at the PSI PHILIPS Cyclotron. The recoiling nuclei of the nuclear reactions with the W target were implanted in a He-atmosphere into variouscatcher foils just behind the target. Ta,

Ti, Pt, Rh, and C served as catcher materials in these experiments. Isotopes of other elements (Ag, As, Se, Te, Y, Ru, Nb, Mo, Ga) were produced due to the interaction of the beam particles with the catcher material. After the long term irradiation (~ 6 h), the catcher foil was placed into the Ta crucible, which was afterwards closed with a Ta-window. The tantalum crucible with an inner diameter of 1.8 cm and a length of 5 cm (model of a future recoil chamber) has a 2 mm hole, which was attached to the inlet of the chromatographic column by a Ta-connector. For the thermochromatographic separations a pure quartz tube or a quartz tube, which was covered inside by thin Au, Ag, Cu, Ni, Pt, and Pd metal foils (see Fig. 1) were used. The quartz tube was then applied to a copper tube. The whole set-up was evacuated by a turbo molecular pump to a pressure of about 5×10^{-5} mbar. An induction heating device was used to heat up the Ta-crucible to about 1800K. This temperature was measured applying an IR thermometer. Along the chromatography column a temperature gradient between 750°C and –170°C was forced by the gradient oven at the starting point and by the cold finger cooled with liquid nitrogen at the end.
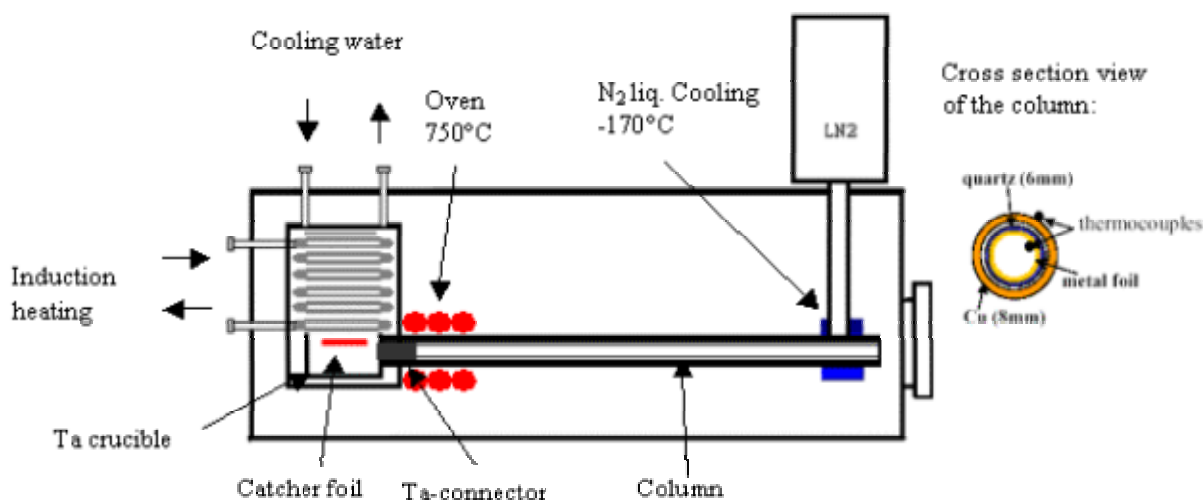

Figure 1. Schematic view of the set-up used for off-line release studies and vacuum thermochromato-graphic experiments.

Each experiment lasted about 30 min. Release efficiencies for volatile elements from the particular catcher material were determined by γ-activity measurement of the given catcher sample before and after heating. The distribution of the elements in the catcher system and their distribution along the chromatography column were determined with a HPGe-γ- detector with a 1 cm lateral resolution applying a lead collimator.

The determined release efficiencies of some volatile species from different catcher materials are compiled in Table 1. Generally, a higher release efficiency may be expected if the working temperature is close to the melting point of the catcher material. We observed a nearly complete release of Pb, Tl, and Bi from the Pt and Rh catcher at a working temperature of 1800K, whereas these elements partly remained in the catcher made of Ta, Ti, and graphite. Despite a He flushing during the irradiation the Ta and Ti catcher were always oxidized in the beam spot. For future applications, Rh was determined to be the best-suited catcher material, since in nuclear reactions of the heavy ion beams with the Pt catcher large amounts of interfering activities (e.g. [211,212]Po) are produced, which disturb the identification of transactinides. All of the released volatile species could be observed deposited in the quartz or metal chromatographic tube. Se was found in the crucible and in the connector, most probably because of the formation of very stable and not volatile Ta-Se compounds. The measured release efficiencies are well

correlated with the release enthalpies $\Delta H_f{}^M$ calculated from the sum and the formation enthalpy of solid solution based on the Miedema model [5] and of the desublimation enthalpy (see Tab. 1). These calculations seem to be very useful for a prediction of release efficiencies for unknown catcher-product combinations. The low release efficiencies for the Ta catcher originated probably from the very low diffusion velocities in a metal with an exceptionally high melting point or from the formation of a Ta_2O_5 layer on the surface of the catcher foil during the irradiation, which may remarkably disturb an efficient release.

Table 1. Release efficiency for some volatile species from different catcher materials.

% {$\Delta H_f{}^M$, kJ/mol}	Catcher/ thickness (μm)	Pt/ 5	Rh/25	Ta/5	Ti/6	C/200	Fe/25
Element	Melting point (K)	2045	2239	3269	1941		1808
Pb		100{281}	88{228}	65{188}	81{298}	70{332}	100{100}
Tl		100{267}	100{211}	58{125}	86{224}	100{324}	{75}
Bi		100{319}	{266}	{237}	{352}	{368}	{138}
Ag		94{288}	30{247}	{225}	62{291}	{348}	{162}
Y		38{763}	67{675}	75{296}	76{350}	67{973}	{429}
Ru		56{661}	{652}	{808}	100{825}	{718}	{677}
Nb		10{986}	9{910}	12{722}	51{714}	41{1168}	{793}
Mo		0{764}	0{717}	0{676}	49{671}	16{900}	{665}
Te			39				
Se							96
As		{493}	{470}	{557}	{622}	{527}	90{433}
Ga		{465}	{421}	{361}	{418}	{531}	87{327}

Adsorption properties of Tl, Pb, Bi, and other volatile species on the metals Au, Ag, Cu, Pt, Pd, and Ni as well as on quartz were determined from the results of the of the vacuum thermochromatography (see Tab. 2). In order to obtain clean metal surfaces, each metal column was pre-treated with the mixture of He and H_2 gas flow at 850°C and then with a pure He gas at the same temperature just before the experiment. The deposition temperatures were determined from the peak maximum of element distribution along the tube. From the experimental parameters the adsorption enthalpies ($-\Delta H_{ads}{}^{TD}$) have been calculated using the thermodynamic model of vacuum thermochromatography from [6,7]. A Monte Carlo simulation based on kinetic model of mobile adsorption [8] was also used to evaluate the adsorption enthalpies ($-\Delta H_{ads}{}^{kin}$) from the experimental results.

Using different catcher materials several determinations of the adsorption enthalpies of Pb and Tl on quartz surfaces were performed. Reasonable reproducibility was found. The determined adsorption data are consistent with data from earlier vacuum thermochromatography experiments ($-\Delta H_{ads}{}^{Lit}$) [7]. In the Pd and Ag column, Pb and Tl were deposited at the starting point. Therefore, only an upper limit of the adsorption enthalpy is given. For the other metal columns, the adsorption enthalpies determined from the present experiment are well comparable with data obtained by gas thermochromatography ($-\Delta H_{ads}{}^{Lit}$) [9].

The developed coupling principle between a catcher system and vacuum thermochromatography was shown to work properly. The chemical inertness, the high release efficiencies at moderate temperatures and the absence of beam induced interfering α-decaying by-products make Rh the most attractive catcher material for future experiments with transactinides. Moreover, extremely stable compounds of Rh with actinide elements are known. Hence, the metal chemistry inside the catcher

material will be valuable for a chemical pre-separation already in the recoil chamber. Such separation effects can be predicted using calculated data of the release enthalpies ΔH_f^M. However, only on-line studies can provide information about the very important kinetics of the release. Therefore, on-line hot-catcher experiments with short-lived isotopes of Hg, Pb, Tl, and Bi using a similar experimental set-up are planned.

Table 2. Deposition temperatures and the evaluated adsorption enthalpies together with values given in literature [7,9]

Catcher / surface	Element	Deposition temperature (K)	$-\Delta H_{ads}^{TD}$ (kJ/mol)	$-\Delta H_{ads}^{kin}$ (kJ/mol)	$-\Delta S_{a, mob}$ (J/mol*K)	$-\Delta H_{ads}^{Lit}$ (kJ/mol)
Rh-02/quartz	Pb	550±25	146±7	154	166	142
Ta-06/quartz	Pb	541±25	142±7		166	
Ta-04/quartz	Pb	589±25	156±7		166	
Ti-02/quartz	Pb	589±25	155±7		166	
Rh_02/quartz	Tl	370±25	98±6	106	167	113
Ta-06/quartz	Tl	465±25	122±6		167	
Ta-04/quartz	Tl	413±25	109±6		167	
Ti-02quartz	Tl	475±25	125±6		167	
Rh_02/quartz	Bi	360±25	96±6	102	168	109
Rh_02/quartz	Ag	648±25	172±8	187	163	
Rh_02/quartz	Se	>1023±25	<271±10	<295	159	
Rh_02/quartz	Te	389±25	103±6	112	165	151
Pt/Au	Pb	931±25	247±12	260	163	229
Pt/Au	Tl	871±25	231±12	240	163	205
Pt/Ag	Pb	>961±25	<254±12	<250	164	
Pt/Ag	Tl	>961±25	<254±12	<250	164	
Pt/Pt	Pb	>1023±25	<271±12	<266	165	
Pt/Pt	Tl	871±25	231±12	226	165	
Pt/Pd	Pb	>1023±25	<271±12	<300	165	326
Pt/Pd	Tl	>1023±25	<271±12	<300	165	326
Pt/Cu	Pb	783±25	207±12	225	168	222
Pt/Cu	Tl	812±25	215±12	235	167	119
Pt/Ni	Pb	931±25	246±12	262	168	227;231; 243;272
Pt/Ni	Tl	389±25	103±6	115	172	117;149
Pt/Ni	Bi	>1023±25	<271±12	<300	168	252; 322; 328; 273
Pt/Ti	Pb	976±25	258±12	264	164	
Pt/Ti	Tl	948±25	250±12	251	164	
Pt/Ti	Zn	842±25	224±12	215	160	

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